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Subcontractor Report

Ultra-Efficient Epitaxial Liftoff Solar Cells Exploiting Optical Confinement in the Wave Limit

Final Technical Report
19 July 1994 — 18 July 1998

E. Yablonovitch
School of Engineering and Applied Science
University of California
Los Angeles, California

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

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NREL Technical Monitor: R. McConnell

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Ultra-efficient Epitaxial Liftoff Solar Cells Exploiting Optical Confinement in the Wave Limit

Final Technical Report

Principal Investigator: Eli Yablonovitch

Epitaxial Liftoff as an Option for Low Cost Solar Cells:

It is now well understood that if GaAs substrates could be re-used for growing epitaxial solar cells, then that would remove a major cost obstacle from high-efficiency terrestrial solar cells. In this project, the epitaxial liftoff approach has been pursued. It leaves a very clean substrate after use, that can be readily re-inserted into an epi-growth reactor. If, as many believe, the epi-growth step can be streamlined and reduced in cost, this would produce the highest possible performance cell, at a cost no higher than other thin film technologies.

While our objectives were quite laudable, our success has not been entirely satisfactory. We have found, as a number of other groups have,[1] that the epitaxial liftoff process is vulnerable to microscopic cleavage cracks in the lifted off films. The larger the area of the lifted off epi-film, the greater the risk of microscopic cleavage cracks. Such cracks block the passage of electricity, and are unacceptable in solar cells. This has restricted us to relatively small area solar cells, which though they performed well, told us very little about scale-up. Among the attached papers is a report of a small thin film GaAs solar cell that performed about as well as a bulk GaAs solar cell would have performed, >20% efficiency.

We don't regard the cleavage cracking problem as fundamental, but within the scope of our University Research project, and with available staffing we were unable to solve that problem.

The issue revolves around the stiffness and stress in the polymer sheet substrate to which the epitaxial film is transferred. After the epitaxial film transfer, the polymer sheet can relax from its originally cured condition when it is bonded to the semiconductor. The resulting polymer strain, can crack the semiconductor epitaxial film, since the semiconductor is quite thin and fragile after liftoff. We believe that this problem could have been overcome if we could develop a polymer production method that leaves no strain behind after the polymer cure. The science of polymers is quite well developed and this is a standard processing problem that would best be solved in an industrial laboratory. We would recommend that as a follow-up project, the issue of optimization of the support polymer layer for the semiconductor film, could be fruitfully and systematically solved. However this is probably not the sort of problem to be resolved at a university.

The problem is exacerbated, since the III-V semiconductor film is usually processed into solar cells prior to the liftoff procedure. Device processing leaves its own strains behind. However these would not be serious provided that the supporting polymer sheet had exactly the same dimensions after liftoff, as before.

Mechanical Support Options for Lifted Off Films.

A group in the Netherlands, has recently published [1] favorable results using a thin evaporated Copper film as a mechanical support layer for the lifted off GaAs. We have tested their approach during this past quarter, and we have found it to be not entirely satisfying. Instead we suggest continuing to use organic polymer layers for mechanical support.

In the past the support layer has been a thick wax layer, or a thick photo-resist layer. We have now switched to very thin <1μm thick photo-resist layers for support that we had not used before. Such a thin layer has much less give to it, and allows much less stretching of the lifted-off film. We have begun to get some of our best crack-free film results using the geometry shown in Figure 1. While it is too soon to call this approach a breakthrough, we are regretful that these results came in so late in this research contract.

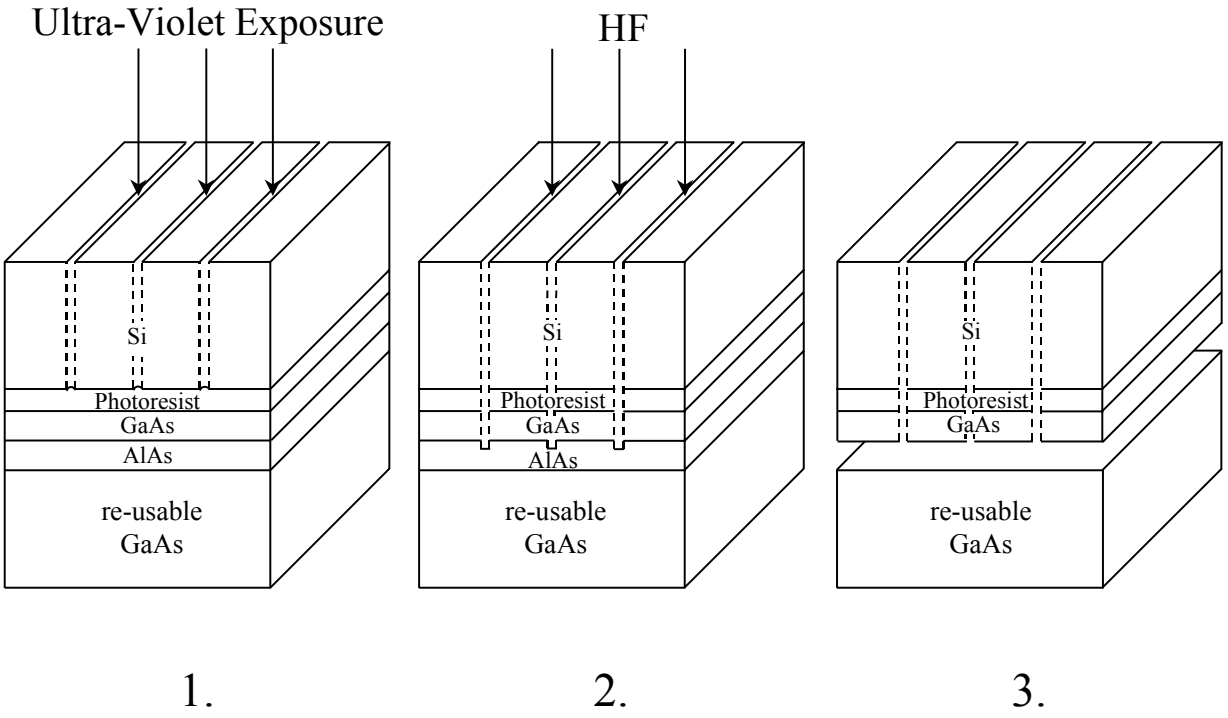

Figure 1: Suggested method for scale up of epitaxial liftoff, and the mechanical support of large area thin films of GaAs.

Figure 1 shows a sequence of three process steps, that has the effect of transferring a thin GaAs epi-layer from a GaAs mother wafer, to a silicon intermediate carrier wafer. The main change from some of our previous processing conditions is that the photoresist layer is very thin, and the silicon support wafer has slots in it, to allow penetration of the HF acid over a large area. The narrow slots are spaced about 1mm apart, and are not regarded as being deleterious to solar cell performance, since long stripe arrays are quite compatible with series-connected module designs, and also with various contact grid options.

In our case, the slots in the silicon support wafer were made by saw cutting. Any other conveniently cut or drilled material, which is acid resistant, could also have been used as the temporary support wafer. Ultimately the GaAs films would be transferred to glass substrates for integration into modules.

The new features represented in Figure 1 are:

1) The photo-resist is much thinner than in our previous work.
2) The process is *self aligned*, in that a positive photo-resist can be exposed by the holes or slots in the support layer, (silicon in this case).

After the photoresist is exposed, it is developed, and a non-selective etch is used to open a channel down to the AlAs that must see the acid for epitaxial liftoff. This is shown in panel 1 of the Figure. Panel 2 shows the HF acid penetrating the slots, and panel 3 shows the separation of the GaAs epi-film from its mother substrate. Some of the problems that have been overcome, other than the crack formation are:

a) Loss of adhesion of the photoresist during the 12-hour acid immersion.
b) Preventing the photo-polymer from clogging the slots.

The first (a) was solved by simply trying a number of different photopolymers. Some brands don't adhere as well as others. The second (b) was solved by the self-aligned exposure method as indicated above. The photo-polymer in the slots was exposed to ultra-violet light, rendering it soluble in the developer, and preventing it from clogging the slots.

We were unable to complete the testing for the mechanical support structure shown in Figure 1. We are not yet certain that the new processing paradigm represented by Figure 1 will completely solve the cracking problem. We believe that testing should continue in the future, and that this approach remains one of the most promising for future photovoltaics, which will have to combine high performance and low cost both. Continued testing of the approach in Figure 1 is recommended in order to gain confidence for scale up. We believe that the overall approach indicated here can be perfected in the context of a government supported research project in an industrial laboratory, rather than in a university setting.

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1. A. van Geelen, P. R. Hageman, G. J. Bauhuis, P. C. van Rijsingen, P. Schmidt, and L. J. Giling, "Epitaxial Liftoff GaAs Solar Cell from a Reusable GaAs Substrate", Mat'ls. Sci. and Eng'g. **B45**, (1997) pp. 162-171.

List and Explanation of Publications:

"Vapor Phase Epitaxial Liftoff Of GaAs And Silicon Single Crystal Films", W. Chang, C. P. Kao, G. A. Pike, J. A. Slone and E. Yablonovitch, Solar Energy Materials and Solar Cells, vol.58, p. 41 (1999)

This paper summarizes what we have learned about epitaxial liftoff of thin, rigidly supported, films, of both GaAs and Silicon. Surprisingly, the acid vapor etchant can penetrate some distance under a film, even if the etching slot is narrow. This is different from the aqueous epitaxial liftoff that had been studied previously. This seems to allow liftoff of large areas, provided that the very narrow etching openings are no more than 1mm apart. It turns out that 1mm is a good width for an individual solar cell stripe in a large series connected panel.

"Absorption Enhancement In Ultra-Thin Textured AlGaAs Films", Boroditsky, M.; Ragan, R.; Yablonovitch, E. . Solar Energy Materials and Solar Cells, vol.57, p.1-7 (1999).

This paper summarizes what we have learned about absorbing solar radiation in an ultra-thin layer of GaAs. It appears that a GaAs layer that is only a few hundred nano-meters thick can still absorb about >80% of the incoming sunlight near the electronic band edge, where absorption is weakest. We did not have the opportunity to fully apply this concept to lifted off solar cells, but we expect that it could be taken into account in future high efficiency designs.

"Non-Destructive Testing By Absolute Room Temperature Photoluminescence Quantum Efficiency Of Gaas Solar Cells", X. Y. Lee, Charles Q. Wu, Ashish K. Verma, Raghu Ranganathan and Eli Yablonovitch, Conference Record of the 25th Photovoltaic Specialists Conference-1996, Washington DC May 13-17, 1996, page 141 (1996).

This paper explains out non-destructive measurement technique for determining absolute room temperature photoluminescence efficiency, before, during, and after solar cell processing. This type of photoluminescence efficiency can be translated directly into open circuit voltage, using basic detailed balancing theories of solar cells.

"Thin Film GaAs Solar Cells On Glass Substrates By Epitaxial Liftoff", X. Y. Lee, Ashish K. Verma, Charles Q. Wu, Mark Goertemiller, and Eli Yablonovitch, Jack Eldredge and David Lillington. Conference Record of the 25th Photovoltaic Specialists Conference-1996, Washington DC May 13-17, 1996, page 53, (1996).

This was a demonstration of the performance of a lifted off GaAs solar cell of rather common design, that did not take advantage of light trapping, and very thin active layers, for example. Nevertheless, the solar cell worked as well as any common GaAs solar cell, and experienced no degradation after epitaxial liftoff. The main disappointment was the small 1mm×1mm size of the cell that could not be scaled up, owing to the risks of micro-crack formation in the lifted off films, as discussed earlier.

Appendices

Attached Preprints of Published Work:

Vapor Phase Epitaxial Liftoff of GaAs and Silicon Single Crystal Films

W. Chang, C. P. Kao, G. A. Pike, J. A. Slone and E. Yablonovitch,

Electrical Engineering Department

University of California, Los Angeles

Los Angeles, CA 90095-1594

ABSTRACT:

Among the technologies for integrating GaAs devices with Si VLSI chips, epitaxial liftoff (ELO) is conspicuous for maintaining the quality of the single crystal epitaxial GaAs films. Traditionally, ELO is implemented in aqueous HF solution. It would be cleaner and simpler if ELO could be implemented in a vapor process. In this article, we will present the potential improvements in the epitaxial liftoff process by using a vapor phase etch to undercut thin films.

Epitaxial liftoff, the separation and manipulation of thin electronic films removed from their substrates, has taken its place among the semiconductor processing and packaging technologies. It relies upon the extreme chemical selectivity which frequently manifests itself in the wet chemistry of organic, inorganic, and epitaxial materials. In this article we explore the prospects of converting epitaxial liftoff (ELO) into a vapor phase process, VELO, hopefully with attendant process simplification.

There have been a great many tests of the effect of the epitaxial liftoff process on lifted off devices [1]. The outcome of all this testing is that, as a general rule, electronic devices are unharmed by the liftoff process. However there is some susceptibility to pinholes in the epitaxial films, and in large area devices such as solar cells, there is a significant risk of forming cleavage cracks. These cleavage cracks are open circuits to current flow, and will leave the solar cells open-circuited or at least very resistive.

The normal cleavage planes in III-V semiconductors are <110> oriented. As free standing thin films, GaAs sheets have very little mechanical strength, and need to be mechanically supported at each stage of the liftoff process. The strength of GaAs is such, that a strain as small as 0.1% can produce cleavage cracks.

The mechanical support can be helpful by supplying compressive stress on the thin GaAs films, or it can be harmful by causing the film to stretch. The films are strong in compression, but weak in tension. During the liftoff, some parts of the film are still attached while other parts are already free. The non-uniformity of these effects tends to put undesirable tensile strains on the films during the liftoff process.

It is now generally accepted that cleavage cracks are the main problem in the application of Epitaxial Liftoff to solar cells. There is some recent work [2] from the Netherlands which addresses some of these problems. They have introduced some significant new innovations:

They cover the GaAs liftoff film with 2-3μm of evaporated Copper metal. This provides both mechanical strength and a favorable thermal expansion co-efficient. Copper contracts more when being cooled from temperatures above ambient, and therefore provides desirable compression on the GaAs film. This allows some tensile stress to be applied during liftoff, which apparently expedites the etch rate. Under-cutting rates on the order of 1mm/hour were demonstrated, which is faster than the normal etch rate ≈0.3mm/hour. We presume that this might be attributed to stress-enhanced corrosion, which is a well-known effect in metallurgy. A single droplet of HF acid applied to the wafer edge provided the undercut etch in the work by van Geelen et al [2].

In this article we will present experimental parametric studies on using acid vapor rather than an aqueous acid for implementing the liftoff process. This permits a cleaner liftoff process, with process simplifications that may assist in addressing the cleavage crack issue. A similar vapor epitaxial liftoff process is presented here for both GaAs/AlAs/GaAs epi-wafers, as well as Si/SiO_2 Silicon-on-insulator wafers.

There have been a number of previous studies of using HF acid vapor for micro-electro-mechanical micro-fabrication and processing steps [3,4]. In addition there have been studies using anhydrous HF vapor [5]. Here we address the effects of acid vapor partial pressure, and its influence on under-cutting speed in comparison to aqueous HF acid.

We have chosen to work with the vapor of concentrated hydrofluoric acid (49%), since it is close to the azeotropic composition, which is where the chemical composition in the vapor

matches [6] that in the liquid. A diagram of our undercut etching apparatus is shown in Figure 1. The typical N_2 vapor flow rates in the 500ml undercutting chamber were 100ml/minute.

Both GaAs and Silicon on SiO_2 (SOI) samples were investigated in this work. The GaAs sample consisted of an N on P $Al_{0.3}Ga_{0.7}As$/GaAs double heterostructure, 1μm thick on a 50nm GaAs ELO etch-stop protection layer, over a 100nm AlAs sacrificial layer on a GaAs buffer layer. The SOI sample consisted of Si and SiO_2 layers with thickness of 330nm and 150nm respectively. All samples were tested under two situations: A rigid backing during liftoff, and a convex undercutting slot during liftoff. The convex films were supported by wax. As they were undercut the tensile stress in the wax would be relieved by inducing a curvature on the semiconductor film, making the etching slot convex. The rigid backing consisted of a silicon chip on a wax adhesive film 1 or 2 μm thick. Under these circumstances the etching slot remained parallel. The etch depth was determined by using adhesive tape to pull off the undercut portion of the films.

We plot the lateral under-cutting rates versus the percentage of saturated vapor, a kind of relative humidity for the acid vapor. One hundred percent of saturation could lead to condensation. Less than 100% of saturation is dry in principle, but the condensation conditions could be quite different in a narrow slot where surface energies influence the condensation equilibrium. Furthermore, since the acid reacts with the AlAs or SiO_2 surface, the reaction products may have a smaller vapor pressure and remain condensed. Therefore the process cannot be regarded as completely dry, even when the vapor pressure is < 100% of saturation. We can assume that sub-microscopic amounts of aqueous acid may be present in the etching slot. In addition, the mass transport conditions might be different in gas phase vapor etching than in aqueous bath etching.

Figure 2(a) shows the initial etch rate of 50nm thick AlAs slots. (All the initial etch rates were measured after one hour in the etchant.) The vapor etch rate is noticeably slower than the aqueous solution point marked on the right hand axis. The scatter is due to non-uniformity in the etch rate. The etch rate is maximum at saturation, but unsaturated vapors were almost equally effective. These etch rates are all slower than the stress-induced etch speedup measured by van Geelen et al [2]. Stress is a double edged sword, and we were trying to avoid the risk of cleavage crack formation.

In Figure 2(b) the cumulative etch rate, after 12 hours is given. Generally the etching slows down in a deeper slot owing to the difficulty of mass transport of reactants and reaction products into and out of the slot. One must assume that the similarity between the aqueous result and the 100% saturation vapor pressure result for the convex slot in Fig. 2(b) is related to the condensation of microscopic amounts of aqueous acid in the slot. Mass transport is somewhat easier in the convex geometry as originally discussed in [7]. Nonetheless, even the plane parallel slot labeled as rigid, allows a 2mm wide stripe to be undercut in 12 hours in aqueous acid. This is surprisingly good in view of the mass transport issues. A large area array consisting of 2mm stripes would be ideal for solar cells, since the stripes would be amenable to series connection, producing a high voltage, and solving one of the packaging problems in solar panels. As mentioned earlier, however, the problem is to prevent cracking in such stripe arrays.

We have also performed vapor ELO measurements on SOI films, as shown in Figure 3(a). The initial vapor undercutting rate is slightly slower than in aqueous solution. However the cumulative rate in aqueous etch comes to a halt at about a 500μm slot depth, to be contrasted with the vapor etch which continues to etch almost linearly with time and doesn't slow down. The mass transport issues for SiO_2 slots are analyzed in [8]. The high solubility of the SiF_4

reaction products should permit the aqueous etching to continue with little slowdown in slots deeper than 500μm. Therefore the halting of the cumulative aqueous etching in Figure 3(b) is puzzling to us, but gratifyingly the vapor etch seems to not have that problem. Again arrays of 2mm wide stripes should be available from SOI wafers. If these could be manufactured, and the substrates re-used, at low cost, then this would also be a possible thin film solar cell option.

We have demonstrated that HF acid vapor epitaxial liftoff is a viable option for separating thin film solar cell material from a parent substrate and is comparable or superior to aqueous acid liftoff. As in all epitaxial liftoff, the separated substrate is in excellent condition and ready to be re-used. The vapor process is essentially dry, except that sub-microscopic amounts of liquid acid might actually be present inside the under-cutting slots.

Large areas of ELO films will be needed for producing significant amounts of photo-voltaic energy. The major problem in the epitaxial liftoff process as applied to solar cells is the scale-up to large area crack-free sheets. Indeed large sheets of many small discrete devices do not present insurmountable ELO problems and large arrays of 1 or 2 mm stripes can be lifted off. But in large area devices such as solar cells, the failure mode turns out to be the risk of cleavage cracks being formed in the lifted off thin films. Crack formation is a stubborn issue that may require new approaches such as those introduced by the Netherlands group [2].

We would like to thank to Thang Chu and Dan Sievenpiper for their assistance. This work was supported by NREL under Contract No. XAL-4-13357-02, and the DARPA Optoelectronic Technology Center.

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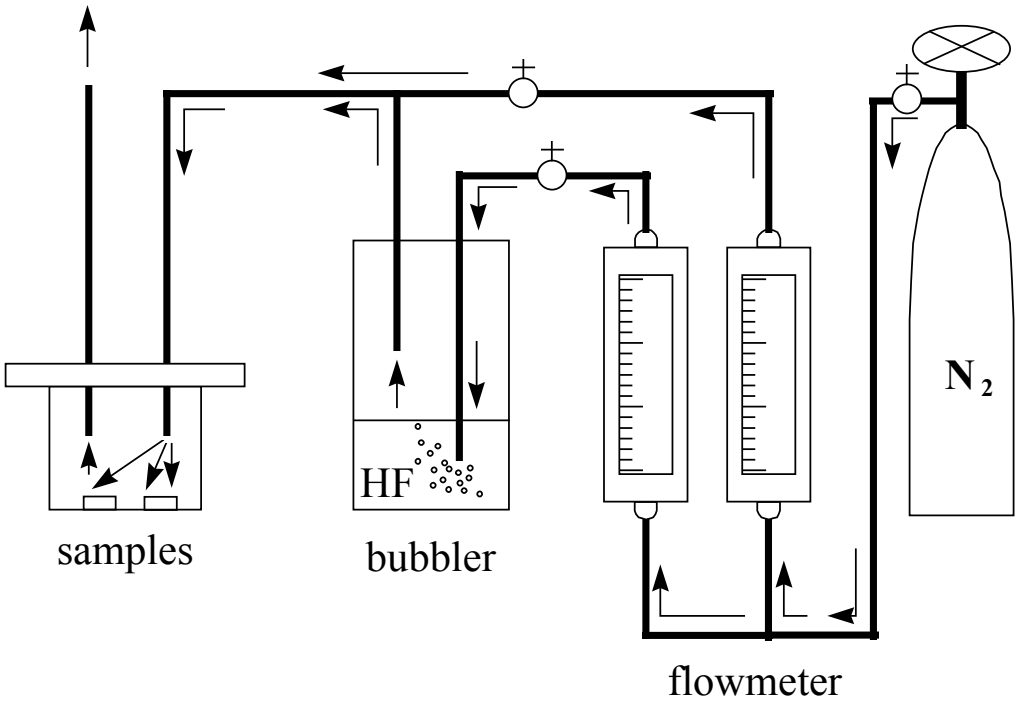

Figure 1: Experimental setup for vapor epitaxial liftoff. The symbols ⏀ represent flow control valves which blend the saturated vapor from the bubbler with dry N_2 to adjust the acid vapor pressure.

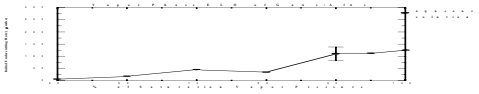

Figure 2(a)

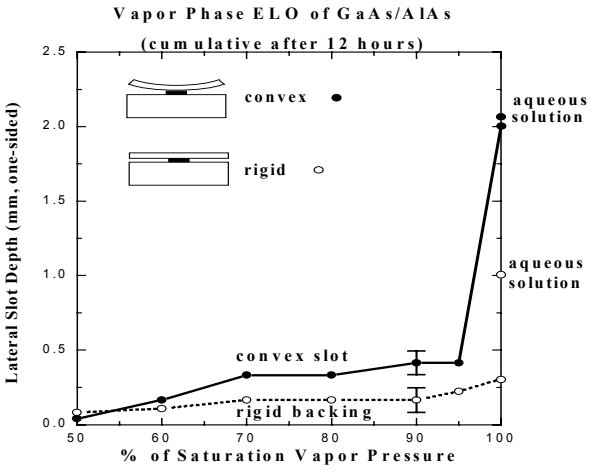

Figure 2(b)

Figure 2(a): Initial lateral under-cutting rates versus the percentage of saturated vapor pressure for GaAs wafers. The aqueous points on the right hand axis represent the corresponding rate for 10 % HF aqueous acid.

Figure 2(b): Cumulative lateral under-cutting distance after 12 hours versus the percentage of saturated vapor pressure, for GaAs wafers. The aqueous points on the right hand axis represent the corresponding distance for 10 % HF aqueous acid.

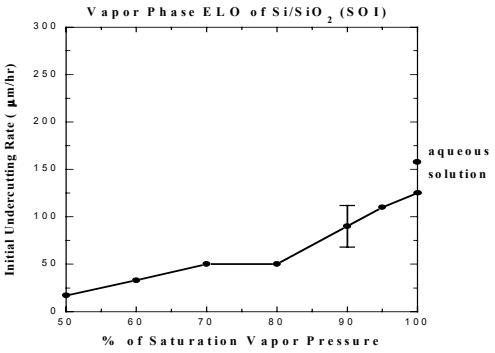

Figure 3(a)

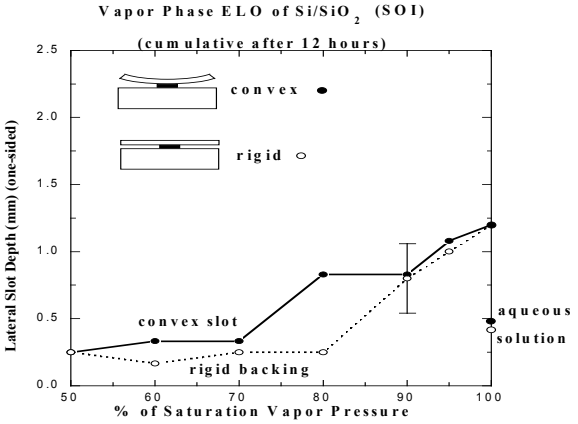

Figure 3(b)

Figure 3(a): Initial lateral under-cutting rates versus the percentage of saturated vapor pressure for SOI wafers. The aqueous points on the right hand axis represent the corresponding rate for 49 % HF aqueous acid.

Figure 3(b): Cumulative lateral under-cutting distance after 12 hours versus the percentage of saturated vapor pressure for SOI wafers. The aqueous points on the right hand axis represent the corresponding distance for 49 % HF aqueous acid.

Absorption Enhancement in Ultra-Thin Textured AlGaAs films

Misha Boroditsky[a], Regina Ragan[b], Eli Yablonovitch[c]

[a]Physics Department, University of California, Los Angeles

[b]Electrical Engineering Department, California Institute of Technology

[c]Electrical Engineering Department, University of California, Los Angeles

Abstract:

We have studied light randomization and the absorption enhancement in textured ultra-thin $Al_xGa_{1-x}As$ films, with a thickness corresponding to a few optical wavelengths. A correlation between the degree of light randomization and trapping, with the scale length of the texturization geometry was found. The observed absorption enhancement corresponds to 90% of the best possible theoretical value, or 90% light randomization. A modified photon gas model is proposed to calculate the light trapping and absorption at the band edge in the textured thin films.

Corresponding author:

Misha Boroditsky
Unversity of California Los Angeles
Electrical Engineering Department
M/S 56-125B, Engineering IV
Los Angeles CA 90095-1594

email: misha@physics.ucla.edu
tel : 310-206-3724
fax : 310-206-8495

It was proposed in late 1970s and early 1980's that light trapping by total internal reflection could be used to increase light absorption in semiconductor wafers. Several techniques were developed, such as natural lithography[1], metal islands[2] and anodical etch of the porous silicon[3] to texturize thin silicon sheets for light trapping. Yablonovitch[4] showed, that in the low absorption limit, total randomization of the light leads to the enhancement of absorption by the factor of $2n_f^2$, where n_f is film's refractive index. This results were confirmed experimentally by Deckman *et al*[5] by applying the natural lithography technique to amorphous silicon films. However, at the moment there is no theory for angular dependence of light scattering from surfaces produced by this process because perturbation methods require that the ratio of roughness height to the wavelength be small[6] while the quasi-classical small slope approximation[7] require a relatively smooth surface.

In this paper we report results of our study of light randomization and absorption enhancement in ultra-thin GaAs/AlGaAs films with a thickness of only a few optical wavelength. The ultra-thin films were textured using the natural lithography while varying the density of cylindrical surface structures. A modified photon gas model, which successfully describes the absorption at the band edge will be presented.

The sample preparation method is by Natural Lithography: A GaAs/AlGaAs double hetero-structure wafer (see Table 1) is patterned with commercially available carboxylate modified 0.95μm polystyrene spheres. The sphere solution is first diluted with methanol to 1% concentration by weight and then surface deposited by dropping a small quantity of a solution on the wafer and spinning the wafer at 1500-2000 rpm. The wafer is spun to distribute the spheres across the surface, and to allow the methanol to evaporate. The

sphere solution concentration and the revolution speed were varied until the conditions were found such that approximately 50% of the wafer area is covered by spheres. From Figure 1a-d, the effect of varying the angular velocity (while holding constant the sphere concentration in solution) on sphere areal density can be seen. The resultant sphere density distribution does not vary significantly across the surface of a given sample. The key point is to avoid building up multiple layers of spheres, which totally coat the surface and provide no patterning.

When the desired sphere distribution is obtained, the sample is etched using the chemically assisted ion beam etching process to transfer a pattern, using the spheres as a lithographic mask. In our work the transferred pattern consists of 0.25μm high mesas, which is approximately 3/4 of the thickness of the top AlGaAs layer. Following etching, the top three epitaxial layers (~1μm) of the wafer, containing the active layer of the device, are removed from the substrate using the epitaxial lift-off procedure (ELO)[8]. The sample is bonded to a glass slide with the untextured side against the glass by using a UV curable polyurethane adhesive. The spectral reflectance, R(λ), of the textured and untextured film was measured over a white surface using a standard integrating sphere setup. Then, absorbance A(λ)of the sample simply becomes:

$$A(\lambda)=1-R(\lambda), \qquad (1)$$

since there is no transmission outside of the sphere. Samples were held horizontally by gravity so that no optically absorbing adhesive materials were necessary inside the sphere. In all our measurements, the probe beam was incident on the glass side with the semiconductor film on the rear, as shown in Fig.2. In this configuration specular reflections from the glass-air and the semiconductor/glass interfaces were identical for the

textured and untextured samples. Thus, changes in reflectivity at the front surface ware not a concern, since the texturing was at the rear surface.

In all the textured samples, an increase in absorption was measured in comparison with the untextured films (see Figures 3&4). The maximum theoretical absorption, which can be attained is ≈80% due to incident beam reflectivity from the glass/air (4%) and semiconductor/glass (16%) interfaces. The best results were attained for samples, which were coated by approximately 50% area coverage of polystyrene spheres and the corresponding 0.25μm high mesas. An absorbance increase from 45% up to ≈75% of a maximally achievable result occurs for the sample in Figure 4 near the band edge. In our best samples, the experimental value nearly reaches the maximum absorbance predicted by theory, as can be seen in Figure 5. The absorbance oscillations, which occur for photon energies above the bandgap, are due to Fabry-Perot fringes. The damping of these Fabry-Perot oscillations in the textured film is an additional evidence of light randomization produced through surface texturization. At energies below the bandgap, free carrier absorption is enhanced from <1% up to the level of ≈20%. Unfortunately, this produces heat rather then electron-hole pairs.

We now describe the photon gas model:

Consider a system consisting of the semiconductor film of thickness d with absorption coefficient α and refractive index n_f attached to a glass slide with the index of refraction n_g (as in Fig. 2). One surface of the film (opposite to the glass) is textured and lies adjacent to the white reflecting surface so that incident monochromatic light enters the film after passing through the glass slide. We assume that all photons which reach the textured surface and white backing are scattered in all upward directions with distribution

function S(θ), where θ is the polar angle. If scattering is perfectly Lambertian, S(θ)∝cosθ. Further, let us call $f_{\uparrow}(\theta)$ the flux density of photons in the film near the textured surface, which are traveling up at angle θ. Due to symmetry, $f_{\uparrow}$ depends only on θ. Also, let $f_{\downarrow}(\theta)$ be a flux of photons in the film near the film/glass interface, which are traveling down at angle θ. In the same manner, $g_{\uparrow}(\chi)$ and $g_{\downarrow}(\chi)$ are defined as the photon flux densities in the glass at the film/glass interface going up and at the glass/air interface going down, respectively (Fig. 2). Reflection at the glass/air boundary gives a relation between $g_{\uparrow}(\chi)$ and $g_{\downarrow}(\chi)$:

$$g_{\downarrow}(\chi)=R_{ag}(\chi)g_{\uparrow}(\chi)\ , \qquad (2)$$

where $R_{ag}(\chi)$ is the reflection coefficient at the glass/air boundary given by the Fresnel formulae. Detailed balance at the glass/film interfaces results in the following relation:

$$g_{\uparrow}(\chi) = f_{\uparrow}(\theta)\exp(-\alpha d/\cos\theta)T_{fg}(\theta) + g_{\downarrow}(\chi)R_{fg}(\theta)\ , \qquad (3)$$

where χ and θ are related by Snell's law. This formula simply states that flux aimed upward in the glass is formed by reflection of photons in the glass from the film/glass boundary and by transmission of the film photon flux, attenuated in the absorbing film, through the same boundary. The same reasoning provides another relation for $f_{\downarrow}(\theta)$ in the semiconductor film:

$$f_{\downarrow}(\theta) = f_{\uparrow}(\theta)\exp(-\alpha d/\cos\theta)R_{fg}(\theta) + g_{\downarrow}(\chi)T_{fg}(\theta)\ . \qquad (4)$$

Also, the upward photon flux at the bottom surface is formed by the scattering of incoming flux and the downward flux of photons on the textured surface. If a monochromatic photon flux of intensity I is incident on the glass surface, to a good

approximation $IT_{ag}(0)T_{fg}(0)(1+R_{fg}(0)R_{ag}(0))$ is transmitted into the semiconductor, and photon flux that reaches the textured surface has intensity

$$I_{tx} = IT_{ag}(0)T_{fg}(0)(1+R_{fg}(0)R_{ag}(0))\exp(-\alpha d/\cos\theta), \quad (5)$$

Since there is no absorption on the bottom surface, the incoming flux must totally balance the outgoing flux. This gives the final equation for the system:

$$f_{\uparrow}(\theta)\cos\theta d\Omega = I_{tx} + \quad f_{\downarrow}(\theta)\exp(-\alpha d/\cos\theta)\cos\theta d\Omega, \quad (6)$$

where integration is performed over 2π steradian. These equations can be solved for any assumed angular distribution of light scattering $f_{\uparrow}(\theta)=S(\theta)$ by integration of Eq. 6 over the solid angles. In the photon gas model in the work of Deckman *et al*[5], an average Lambertian length for absorption is used. This is not valid for the strongly nonlinear dependence of absorption on the propagation angle. Our theory, being more general, explicitly takes into account absorption of photons scattered at different angles. Instead of assumption of totally randomized photons, the model can deal with any angular dependence of scattering, such as Lambertian in this paper. It can also accommodate a dependence on incoming beam incidence angle. Instead of treating the freestanding film, the sample is treated as bonded on the glass or sapphire slide, thus taking into account a practical problem of the light trapping in the supporting slide.

Given this photon gas model, the amounts of reflected and absorbed light can be calculated. Knowing the absorption spectrum of the film and its dispersion, one can obtain the full spectral dependence of absorbance of the textured semiconductor film bonded to a glass slide. Since the samples we studied contained various $Al_xGa_{1-x}As$ alloy layers, the absorption coefficient α and the refractive index n_f in the above formulas are

average values weighted by the thickness of the corresponding layers. The calculated absorbance dependence for perfect Lambertian texturing is presented in Figure 5 along with the experimental curve. Two curves show good agreement leading us to believe that in the samples which have approximately 50% of the surface area covered by 0.25μm high mesas at least 90% perfect light randomization has been achieved.

We have studied light randomization and absorption in AlGaAs films textured by means of natural lithography. A reproducible thin film fabrication process was developed that provides 90% of ideally predicted band-edge absorption relative to our theoretical model. Since the 1μm diameter spheres are visible in the optical microscope, natural lithography with this sphere size is easy to monitor and optimize. Our technique is applicable for fabrication of thin film solar cells and LED's based on III-V compounds. Epitaxial lift-off technology allows us to fabricate very thin AlGaAs solar cells[9], making them lighter and cheaper and providing higher operating point voltages.

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Structure of the GaAs/AlGaAs quantum well wafer

GaAlAs	0.32 μm	window layer
GaAs	0.20 μm	active layer
GaAlAs	0.44 μm	window layer
AlAs	0.05 μm	sacrificial layer
GaAs	>100 μm	substrate

Table 1.

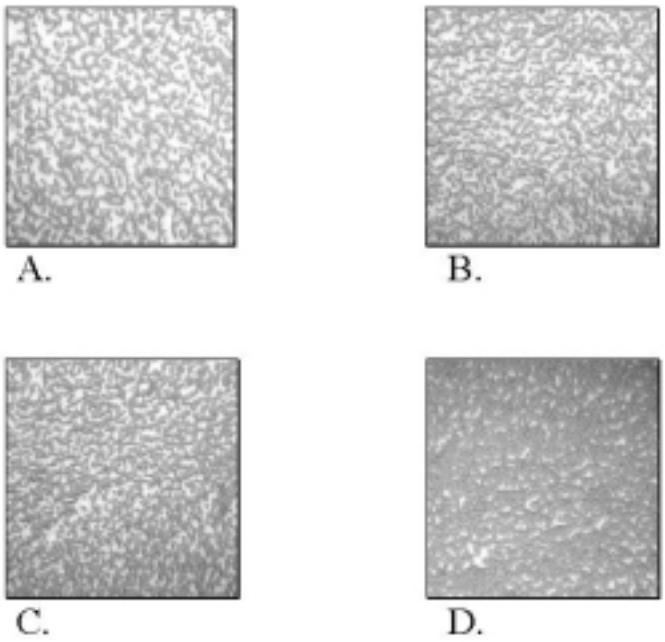

Figure 1.

Figure 1:
Variation of sphere density with angular velocity. The concentration is 30 drop of sphere solution in 1.5ml of methanol. The darker area represents spheres. The spheres tend to cluster at higher surface concentrations.

a. Sphere distribution for 1800 rpm.
b. Sphere distribution for 1700 rpm
c. Sphere distribution for 1600 rpm
d. Sphere distribution for 1550 rpm

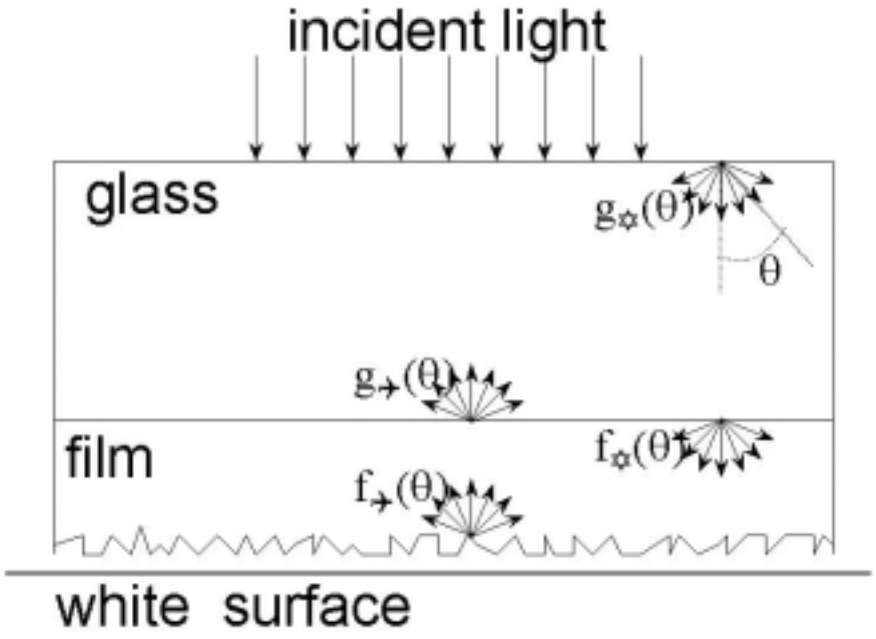

Figure 2.

Figure 2:
Experiment configuration and definition of terms used in modeling

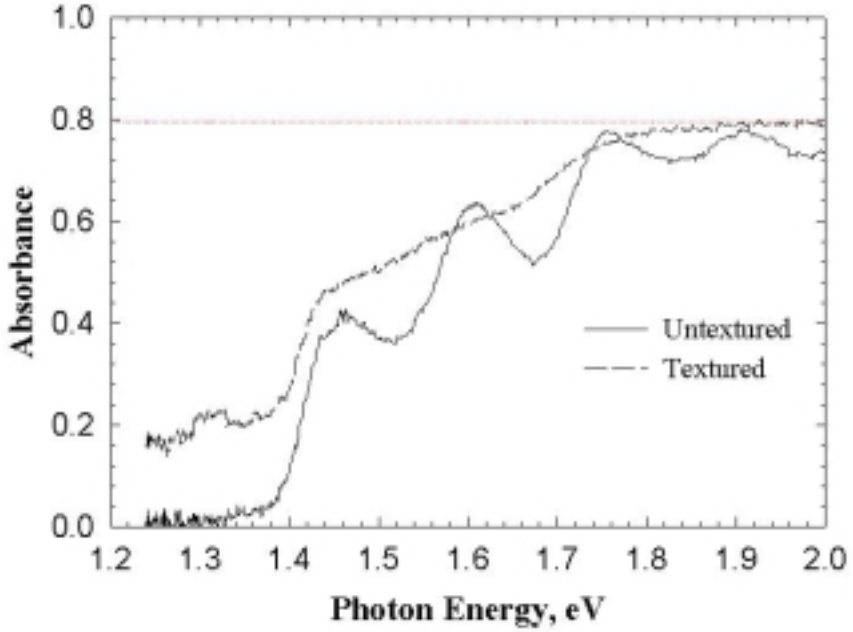

Figure 3.

Figure 3:
Sample with the sparse distribution of spheres. The absorption enhancement is minimal.

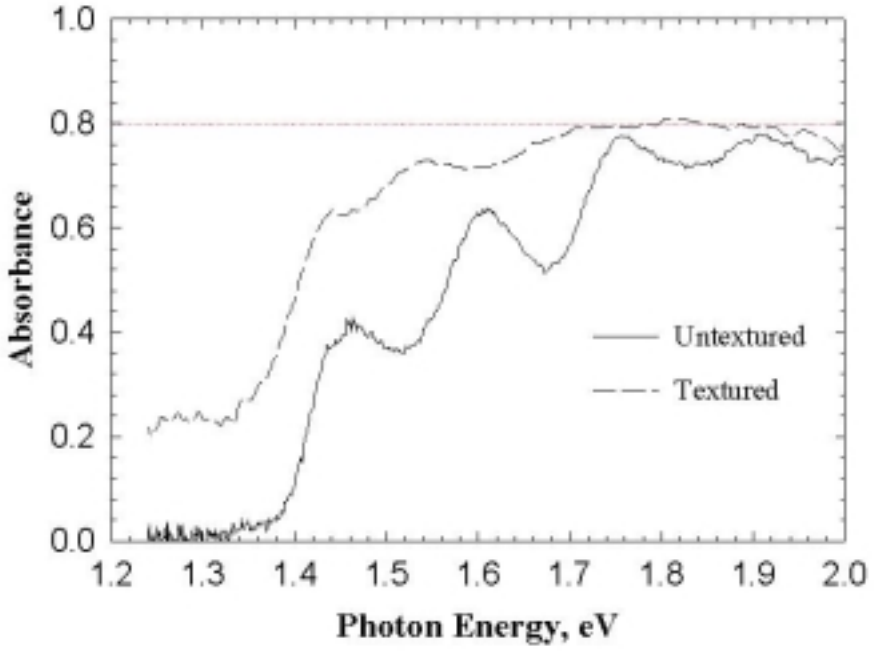

Figure 4.

Figure 4. Sample with 50% of the surface area covered with spheres. A large absorption enhancement is obtained near the band edge.

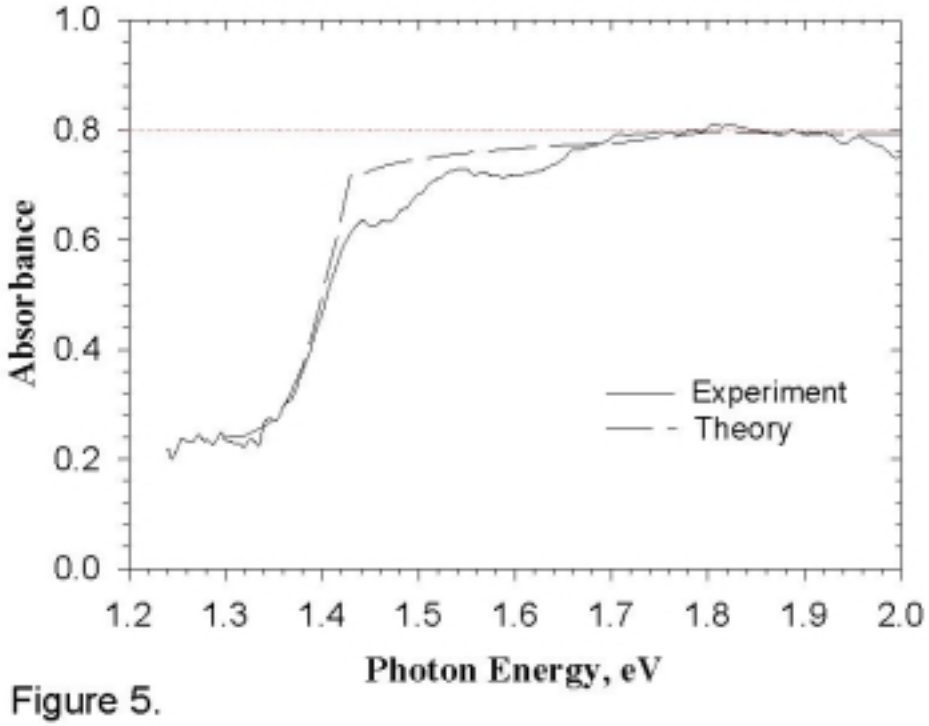

Figure 5:
Comparison between the maximum theoretical absorption for a textured film and the values obtained experimentally.

NON-DESTRUCTIVE TESTING BY ABSOLUTE ROOM TEMPERATURE PHOTOLUMINESCENCE QUANTUM EFFICIENCY OF GaAs SOLAR CELLS

X. Y. Lee, Charles Q. Wu, Ashish K. Verma, Raghu Ranganathan and Eli Yablonovitch
Department of Electrical Engineering,
University of California, Los Angeles

INTRODUCTION

Nondestructive room temperature photoluminescence (PL) measurements on semiconductors are an important characterization tool to evaluate material quality and study the opto-electronic conversion mechanism involved in devices such as light-emitting diodes, solar cells, etc. [1, 2]. In this paper, we will describe non-destructive PL characterization studies of partially processed GaAs solar cells. Such a tool is valuable in process development of high performance solar cells.

EXPERIMENTAL SETUP

The experimental procedure employed for absolute calibration is similar to that in Reference 1, with the PL from the active layer being referenced against the scattered light from a reflective Lambertian white surface placed in the identical optical set up, as shown in Figure 1.

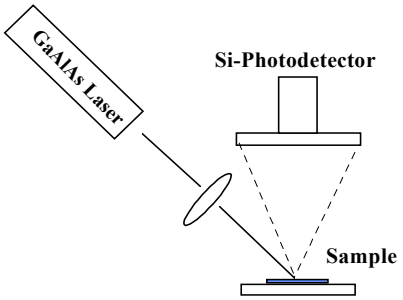

Fig 1. Experimental PL set-up.

An AlGaAs laser (780nm) was used as a pump source, and photoluminescence at 880nm was collected by a Si-photodetector through a 830nm long pass color filter. A conventional p-AlGaAs/n-GaAs/AlGaAs double heterostructure was grown over a 500-Å-thick AlAs release layer by organometallic chemical vapor deposition, as shown in Figure 2 [3].

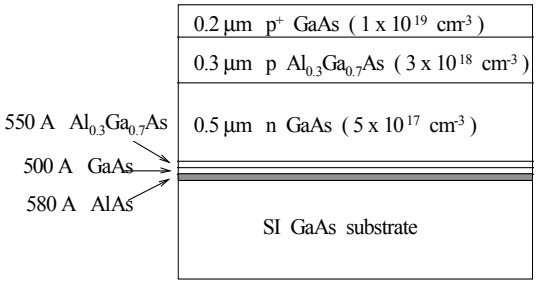

Fig. 2 Heterostructure for the GaAs Solar Cells.

CALIBRATION

For efficiency calibration purposes, we used a simple optical model for the known absorption and reflection from a GaAs substrate. Internal quantum efficiency η_{int} was evaluated from the measured value for the external efficiency η_{ext}, which is given by the relationship:

$$\eta_{ext} = V_{PL} / (T_1 T_2 T_F A_p C V_{White})$$
$$\eta_{int} = 4n^2 x\eta_{ext} \quad \text{(if the escape angle is small enough)}$$

where the measured PL output signal V_{PL} is referenced to the fraction of the input absorbed by the active layer. T_1 and T_2 are the Fresnel transmission coefficients of pump light going in and PL coming out of the medium. T_F is the photoluminescence transmission of the pump blocking filter. A_p is the absorption term which is equal to 1-exp(-aL), where a is the absorption coefficient and L is the thickness of the active n-GaAs layer. C is the correction factor ≈ 1, for the difference of responsivity of the photodetector at the luminescence wavelength 880nm and the pump wavelength 780nm. V_{White} is the scattered signal of the reference white surface whose reflectivity is unity. For a plane surface, the escape cone of only 16°, imposed by Snell's law, covers a solid angle of only ≈ $(1/4n^2)\times 4\pi$ steradians. Because the refractive index at 880nm is about 3.5 for GaAs, the external efficiency would be ≈ 2.0% for internal efficiency of 100%. From the measurements, the internal

efficiency was found to be ≥ 90% which indicates the good quality of the sample.

PREDICTING J_c

From the luminescence efficiency versus pump intensity we can determine the I-V curve. As shown in Figure 3,

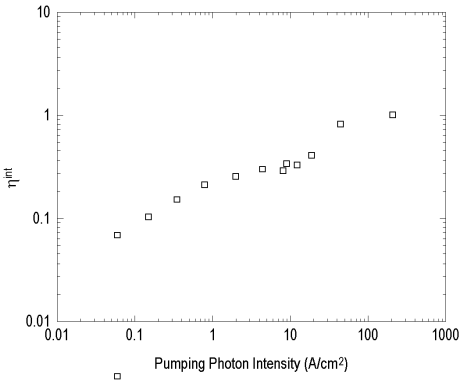

Fig 3. Internal quantum efficiency h_{int} from PL measurements of the GaAs heterostructure with different pumping photon-intensity.

the PL signal decreases below 50% when the excitation photo-current density is $J_c \approx$ 5-50 A/cm^2. J_c represents the cross-over transition from radiative recombination to non-radiative recombination. Electrically, the transition point from the electrical diffusion regime (low-injection) to the recombination regime is $J_c = (J_{02})^2 / J_{01}$, where J_{01} is the pre-factor of the n = 1 radiative current and J_{02} is the pre-factor of the n = 2 non-radiative current. The narrow-base diffusion model gives us a saturation current of diffusion $J_{01} \approx 1.3\times10^{-20}$ A/cm^2. Therefore, plugging J_{01} and J_c into the above equation, we obtain optical $J_{02} \approx 2.5\times10^{-10}$ - 8.0×10^{-10}A/cm^2. From the I-V curve of the fully processed solar cell diode, electrical J_{02} is observed to be $\approx 4.3\times10^{-10}$A/cm^2. This value lies within the range predicted from the PL data, indicating good qualitative agreement between the optical and electrical measurement techniques.

ETCHING RATE CALIBRATION

A simple application of our approach is to calibrate etch rates and epi-layer thickness. We rely upon the efficiency drop when the wide bandgap hetero-layers are removed by etching. To characterize the sample, we used H_2SO_4:H_2O_2:H_2O (1:8:500) to non-selectively etch a small piece cut from the wafer. The PL intensity was measured after every 30 seconds of etching, as shown in Figure 4.

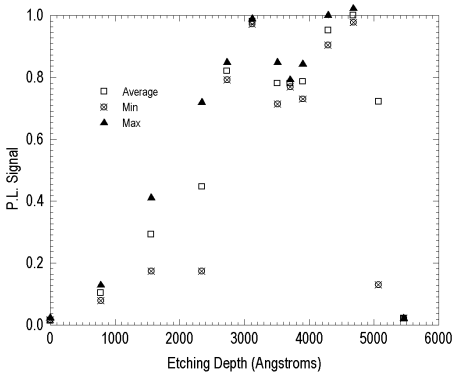

Fig 4. PL measurements of the GaAs heterostructure during the etching.

The final drop in this plot is due to the loss of carrier confinement when the cladding layer (p-AlGaAs) is etched and removed.

SUMMARY

In summary, we have performed contactless photoluminescence characterization of GaAs solar cells. Besides the calibration of absolute internal quantum efficiency, J_{02} from PL characterization is 2.5×10^{-10} - 8.0×10^{-10}A/cm^2 compared with 4.3×10^{-10}A/cm^2 from the electrical I-V curve. These preliminary results show that contactless absolute PL characterization is a useful tool for process development of solar cells.

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THIN FILM GaAs SOLAR CELLS ON GLASS SUBSTRATES BY EPITAXIAL LIFTOFF

X. Y. Lee, Ashish K. Verma, Charles Q. Wu, Mark Goertemiller, and Eli Yablonovitch
Dept. of Electrical Engineering, University of California at Los Angeles, Los Angeles, CA 90095

Jack Eldredge and David Lillington
Spectrolab, Inc., Sylmar, CA 91342

ABSTRACT

In this work, we describe the fabrication and operating characteristics of GaAs/AlGaAs thin film solar cells using the epitaxial liftoff (ELO) technique. This technique allows the transfer of these cells onto non-absorbing glass substrates, and makes possible light-trapping operation. The enhanced performance of the lifted-off solar cell is demonstrated by means of electrical measurements under both dark and illuminated conditions.

INTRODUCTION

In recent years, III-V solar cell technology has been actively pursued for use in space applications. This is due, in large part, to the superior efficiency of these materials, compared to silicon. Attention has also been given to the fabrication of thin film cells, due to their potential for reduced weight and cost, and improved efficiency [1,2]. As a result, III-V cells show significant potential for terrestrial use as well. In this work, we describe the fabrication and operating characteristics of GaAs/InGaP thin film solar cells using the epitaxial liftoff (ELO) technique [3]. This technique allows the transfer of these cells onto non-absorbing glass substrates, and makes possible light-trapping operation with enhanced performance.

DEVICE FABRICATION AND LIFTOFF

The structure used in our experiment (see Fig. 1) was grown using metal organic chemical vapor deposition. It consists of an n-GaAs active region sandwiched between $In_{0.49}Ga_{0.21}Al_{0.3}P$ and $In_{0.49}Ga_{0.51}P$ window/passivation layers, and capped by a p^+-GaAs contact layer. The entire structure is grown on top of a 500 Å thick sacrificial layer of AlAs, which is subsequently etched to release the device from its substrate. A thin GaAs layer above the AlAs serves to protect device layers during liftoff.

Devices were fabricated by first depositing Cr/AuZn/Au p-type contacts onto the sample, followed by a mesa etch down to the n-type active region. After the evaporation of AuGe/Ni/Au contacts onto the active region, the sample was annealed at 380°C, to make the contacts ohmic. The material and junction quality were monitored after each process step using nondestructive room temperature photoluminescence [4] and open-circuit voltage (V_{oc}) testing. No reduction in V_{oc} was observed during the process sequence, indicating minimal parasitic leakage in the junction.

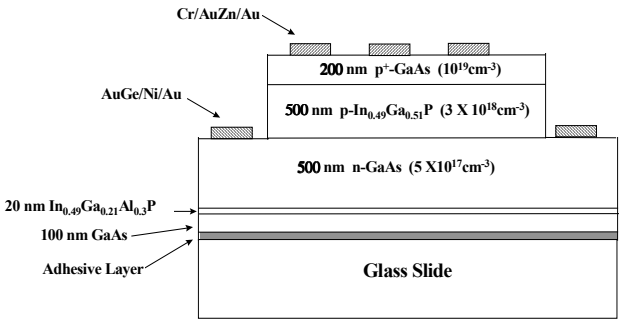

Fig. 1 Structure of the p-n GaAs solar cell.

After device fabrication, the sample was covered with black wax, as shown in Fig. 2. The thin film was lifted off of its substrate by selectively etching the AlAs layer in HF acid solution, and attached to a glass substrate with UV-curing polyurethane. The black wax was then dissolved using trichloroethylene (TCE), after which conductive brass wires were attached to the p- and n-type contacts.

ELECTRICAL MEASUREMENTS

Electrical measurements were then performed on the lifted-off solar cell. The dark current-voltage (I-V) characteristic is shown in Fig. 3. This plot exhibits a diode factor of n=1.93 for voltages between 0.45 V and 0.9 V, which corresponds to nonradiative recombination current. The I-V curve is virtually identical to that obtained before liftoff, indicating little material degradation during that step. It is desirable for the operating point of the cell

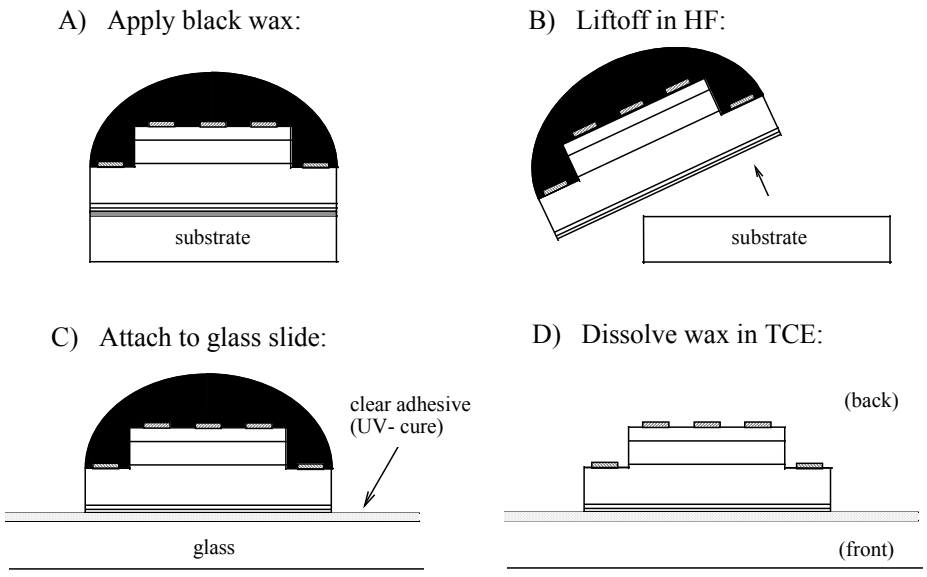

Fig. 2. Epitaxial liftoff process

to occur in the n=1 radiative recombination current regime, which is encountered at higher voltages. In the figure, however, this current is obscured by series resistance.

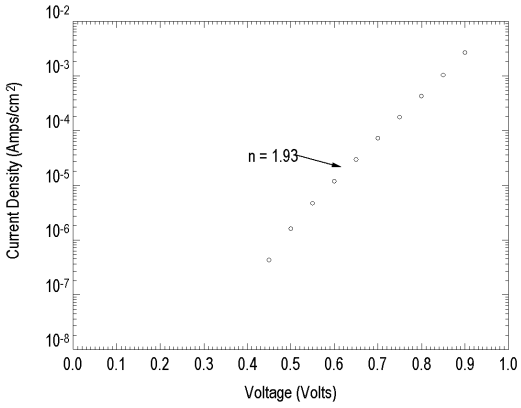

Fig. 3. Current-Voltage characteristic in the dark.

I-V curves were also obtained under an illumination condition of 1 sun (AM0). The above solar cell is bifacial, in that it can be illuminated either through the glass slide (the "front" side) or from the contact ("back") side. The result of the measurement is shown in Fig. 4. Illumination from the front yields V_{oc}= 0.995 V and a short-circuit current I_{sc} of 30.7 mA/cm^2. At an operating voltage of 0.85 V, the fill factor of this characteristic is 77% The improved performance in this configuration is due to the fact that incident light is not obstructed from the active region by metal contact pads. Moreover, reflection from the pads on the backside may enhance performance by recycling unabsorbed photons.

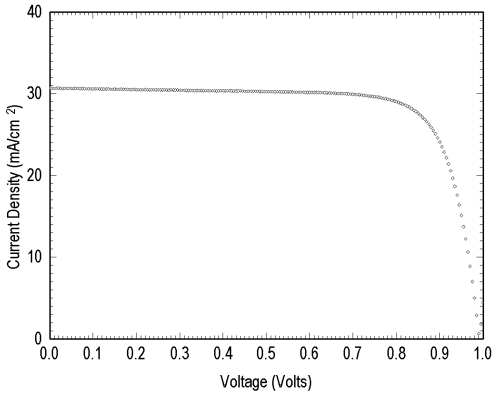

Fig. 4. Current-Voltage characteristic under 1-sun (AM0) illumination from the front side of the solar cell.

DISCUSSION

Referring to Fig. 3, it can be seen that the operating point lies in the undesirable n=2 region of the I-V characteristic. This can be partially attributed to the high series resistance (»350 Ω) in this diode, the primary source of which is the sheet resistance of the lightly doped n-type active region. Another critical factor is the bandgap of the $In_{0.49}Ga_{0.21}Al_{0.3}P$ window layer. This layer was made with a low Al-content, in order to prevent its degradation during the sacrificial etch step. Consequently, a large amount of solar radiation is absorbed and lost in these layers before reaching the active region. The result is a reduction in both V_{oc} and I_{sc}, which also tends to move the operating point into the n=2 regime.

We have made a decision that future practical production of solar cells will require a InGaAlP layer with < 30% Al concentration to avoid attack by HF. Composition with > 50% are feasible in a small area device, but would be susceptible etching through pin-holes in the protective GaAs layer.

CONCLUSION

In summary, we have integrated a working thin film GaAs solar cell onto a glass substrate, using the epitaxial liftoff technique. This configuration allows illumination through the non-contact side of the cell, which increases its collection area and short-circuit current. The cell exhibits V_{oc}= 0.995 V and I_{sc}= 30.7 mA/cm^2. These values are limited by series resistance and absorption in the window/passivation layers. By addressing these issues, it is expected that performance can be significantly improved.

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6. AUTHOR(S)
E. Yablonovitch

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of California, Los Angeles
School of Engineering and Applied Science
Electrical Engineering Department
Box 951594
Los Angeles, CA 90095-1594

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13. ABSTRACT *(Maximum 200 words)*

This report describes work performed by the University of California during this subcontract. In this project, we pursued the epitaxial liftoff approach, which leaves a very clean substrate after use that can be readily reinserted into an epi-growth reactor. If, as many believe, the epi-growth step can be streamlined and reduced in cost, this would produce the highest possible performance cell, at a cost no higher than other thin-film technologies. We have found, as a number of other groups have, that the epitaxial liftoff process is vulnerable to microscopic cleavage cracks in the lifted-off films. The larger the area of the lifted-off epi-film, the greater the risk of microscopic cleavage cracks. Such cracks block the passage of electricity and are unacceptable in solar cells. This has restricted us to relatively small-area solar cells, which though they performed well, told us very little about scale-up. In the area of lifted-off films, a group in the Netherlands has recently published favorable results using a thin evaporated copper film as a mechanical support layer for the lifted-off GaAs. We have tested their approach during this past quarter, and we have not found it to be entirely satisfying. Instead, we suggest continuing to use organic polymer layers for mechanical support. In the past, the support layer has been a thick wax layer, or a thick photo-resist layer. We have now switched to very thin <1-μm-thick photo-resist layers for support. Such a thin layer has much less give to it, and it allows much less stretching of the lifted-off film.

14. SUBJECT TERMS
photovoltaics ; low-cost solar cells ; epitaxial liftoff ; GaAs ; ultra-efficient solar cells

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